

Use of DiaCell modules for the electro-disinfection of secondary-treated wastewater with diamond anodes

Anaid Cano¹, Carlos Barrera¹, Salvador Cotillas², Javier Llanos², Pablo Cañizares²,
Manuel A. Rodrigo^{2*}

(1) Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón
intersección Paseo Tollocan S/N, C.P. 50120, Toluca, Estado de México, Mexico

(2) Department of Chemical Engineering. Facultad de Ciencias y Tecnologías
Químicas. Universidad de Castilla-La Mancha. Campus Universitario s/n. 13071
Ciudad Real. Spain

**Corresponding author: Manuel.Rodrigo@uclm.es*

Abstract

In this work, the disinfection of the effluent of the secondary treatment of a municipal wastewater treatment plant is studied using two stacks of commercial electrochemical cells powered with very low current densities ($0.14 - 10 \text{ A m}^{-2}$), in order to prevent the formation of chlorates and perchlorates during the electrolysis. Results demonstrate that this technology is robust and efficient and it can attain the complete disinfection of wastewater even at very low current densities. These low current densities are high enough to produce hypochlorite and chloramines (when ammonium is present in solution), being the disinfection process more efficient when the concentration of chloramines is higher. Therefore, the presence of hypochlorite together with higher concentrations of chloramines significantly improve the removal of microorganisms. In comparing the two stacks studied in this work, it was obtained that commercial DiaCell

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stacks containing bipolar connected electrodes are more efficient than those containing monopolar-connected electrodes for the disinfection. Differences are explained in terms of the higher cell voltage applied in that stack (higher current density in bipolar stack) that results in (1) an improved reduction of nitrates to ammonium (BDD cathode in bipolar stack) with the latter formation of chloramines as the main positive effect and (2) in the increase in the power consumed as the primary negative consequence.

Keywords

Disinfection, electrolysis, diamond electrodes, scale-up, stacks

Highlights

- Disinfection of secondarily-treated wastewater can be attained by electrolysis with diamond electrodes
- Significant differences between the results obtained with two DiaCells stacks despite using the same anodes
- For the same total current, higher efficiency in the disinfection attained by cell equipped with bipolar electrodes
- For the same total current, lower energy consumption in the disinfection attained by cell equipped with monopolar electrodes

Introduction

Disinfection using electrochemical technology is becoming a hot topic nowadays [1-5]. Recent papers demonstrate that it is a more than promising technology with results that currently overcome limitations of other widely used technologies [6-15]. There are several approaches to attain the electro-disinfection (ED) of water or wastewater, such as, UV disinfection, ozone, chlorine... One of the most interesting is that based on the direct electrolysis of the water (or wastewater) to be disinfected without the further addition of chemicals, as occur in conventional disinfection processes [16]. In that case, disinfection is based on the production of oxidants from the oxidation of anions directly contained in the raw water or wastewater, such as chloride, sulfate, phosphate or carbonate.

Depending on the composition of water or wastewater, use of the proper anode material may favor the formation of powerful oxidants during the electrolysis, which can attack microorganisms and help to remove them from solution. Hence, it is known that Dimensionally Stable Anodes (DSA) containing ruthenium oxides promotes the formation of chlorine and hypochlorite in water [17, 18] while the boron doped diamond (BDD) anode promotes the formation of peroxospecies such as peroxosulfates, peroxophosphates and peroxocarbonates [19]. These latter highly-desired species are not formed by DSA-RuO₂ anodes, and this fact becomes a clear disadvantage for this anodic material. However, DSA also shows clear advantages over diamond coating in disinfection such as the lower price of the electrodes and the prevention of the formation of the undesired chlorates and perchlorates [20, 21]. As it is well known, both species have become the worst drawback of diamond electrodes in this very important health-related application [22-25]. Prevention of the formation of these oxidants is not an easy task and currently there are two main routes of study:

- use of hydrogen peroxide to react directly with the formed hypochlorite, preventing the further oxidation to chlorates and perchlorates [26] and
- application of low current densities in order to prevent electrochemically the formation of chlorates and perchlorates in the treated water [27].

In comparing the disinfection of water and wastewater, a clear indication appears for wastewater, because it normally contained ammonium or nitrates ions [28]. In the second case, the cathodic reduction transform nitrates very efficiently into ammonium and this ion is known to react chemically with hypochlorite forming chloramines, which are powerful disinfectants [29, 30]. This mechanism has also shown to be very important to prevent the formation of chlorates and perchlorates and it has also revealed interesting to prevent the formation of hazardous organo-chlorinated species.

In order to have a complete view of the ED of raw water or wastewater, it is also important to take in mind that, in addition to the anodic production of oxidants from anions contained in the water or wastewater to be disinfected, other two processes should be accounted to explain the high efficiency of the ED processes:

- the cathodic production of hydrogen peroxide by reduction of the oxygen produced anodically (which typically saturates water during electrolysis) [31, 32] and
- the formation of other oxidants such as ozone [19, 33]

One of the points to be further studied in the next years in electrolysis [2, 34] is the scale-up of the technology. Although every year hundreds of papers are published related to electrolysis with diamond electrodes, very few papers are focused on the scale-up of the technology in order to get know-how about the potential use of the technology in full-scale applications [35]. In previous work of this group, it has been

studied first stages in the scale-up of the conductive diamond electrochemical oxidation by evaluating two different types of electrochemical stacks in the electrolysis of effluents polluted with pesticide 2,4-D [36]. In particular, the effect of the monopolar and bipolar connection of electrodes demonstrated to be a very important point to be considered in further studies. At this point, it is worth to take into account that nowadays there are very few works focused on the use of large-size commercial cells for environmental applications. Most of the studies are carried out at lab-scale [34, 35] and it is now demanded more knowledge about the application of the technology at higher scale, using commercial devices, which is a major advantage because results can be then more easily extrapolated to full-scale applications.

On this basis, this work aims to extend the conclusions of this previous study about the oxidation of organics contained in wastewater to the electrochemical disinfection of wastewater with diamond electrodes. The strategy used to minimize and/or avoid the formation of chlorates is the application of very low current densities. Under those conditions, performance of commercial stacks DiaCell Type 401 and DiaCell Type 1001 is to be compared. The first type of electrochemical stack used bipolar electrodes while the second uses monopolar connected electrodes. Both stacks are specially designed for the electrochemical treatment of water and wastewater, by considering the proper flow of liquid and stripping of gases produced, opposite to many other types of commercial cells used for this application but initially designed for electrosynthesis and not for environmental applications.

Materials and methods

Experimental procedure and setup

Wastewater used in this work is an effluent of the secondary clarifiers of the municipal WasteWater Treatment Plant (WWTP) of Ciudad Real (Spain). This plant treats the wastewater produced in an average-sized town (75,000 inhabitants) located in the center of Spain without a significant industrial contribution. The main characteristics of the samples are shown in Table 1.

Table 1. Wastewater average composition.

Parameter	Value
Chloride (mg dm ⁻³)	165
Nitrate (mg dm ⁻³)	8.72
Sulphate (mg dm ⁻³)	261.85
Ammonium (mg dm ⁻³)	0.30
TOC (mg dm ⁻³)	14.95
COD (mg dm ⁻³)	25
<i>E. coli</i> (CFU 100ml ⁻¹)	5400-9100
pH	7.85-8.25
Conductivity (μS cm ⁻¹)	1150-1250

TOC-Total Organic Carbon
COD-Chemical Oxygen Demand

All experiments were conducted in a DiaCell® type 401 or a DiaCell® 1001, both stacks supplied by Adamant Technologies (Switzerland) (nowadays this company does not longer exist and the cells are sold by WaterDiam, France) (Figure 1). The experiments were carried out at constant current (galvanostatic conditions) and discontinuous mode. The total volume treated was 4 dm³ and the electrolysis time was 3 hours. The flow rate used in all the experiments was 50 dm³ h⁻¹. The DiaCell® type 401 module can be assembled with one, two, three and four compartments, each of them being fed with wastewater by internal parallel inlets. The boundary electrodes are

monopolar Si/BDD and in case of using multiple compartments, the separating electrodes are floating bipolar Si/BDD electrodes. All electrodes are circular (100 mm diameter) and the inter electrode gap is 1 mm. The DiaCell® type 1001 is a module with 1-10 compartments equipped with BDD electrodes as anodes and five stainless steel plates; each plate serves as a common cathode for two parallel BDD anodes. In each compartment, a pair of Si/BDD and stainless steel electrodes with an active surface of 70 cm² behaves as a unit cell.

Regarding the BDD electrodes, resistivity of the Si wafers was 100 mΩ cm and the thickness of the BDD coatings was 2-3 μm. Boron concentration in the coatings was 500 ppm and the ratio sp³/sp² around 150. Prior to electrolysis assays the BDD electrodes were cleaned during 10 min in a 1 M Na₂SO₄ solution at 30 mA cm⁻². Mass transfer coefficients have been determined using the ferro-ferricyanide test for the different stacks studied for the DiaCell ® 1001 at the flowrate used in the experiments, following the procedure described by elsewhere [37]. The values obtained were within the range of 2.16 to 7.16 10⁻⁶ m s⁻¹.

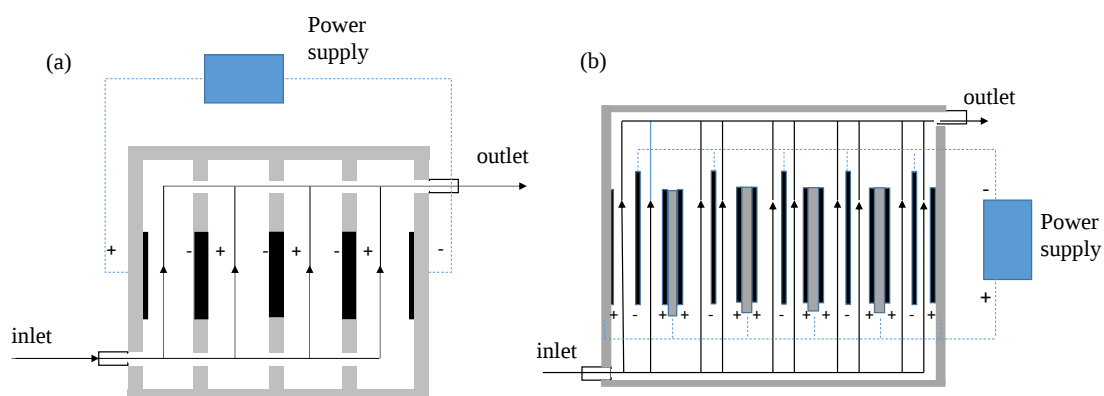


Figure 1. Scheme of the two stacks evaluated in this work (a) DiaCell® type 401 (bipolar connection) (b) DiaCell® type 1001 (monopolar connection).

Analytical techniques

Escherichia coli (*E. coli*) cells were estimated by the most probable number (MPN) technique [38] (confidence level: 95%). Microorganisms were diluted (1:10, 1:100, and 1:1000) and incubated during 24 h at 44°C using 5 tubes at each dilution. The media culture used was E.C. MEDIUM ISO 7251 (the composition of the medium per liter of distilled water was 20 g L⁻¹ tryptose, 5 g L⁻¹ lactose, 1.9 g L⁻¹ bile salts n°3, 4 g L⁻¹ K₂HPO₄, 1.5 g L⁻¹ KH₂PO₄ and 5 g L⁻¹ NaCl) provided by Laboratorios Conda (Spain). For the determination of *E. coli*, 37.4 g of this reactive was dissolved in M-q water and were sterilized at 121°C during 10 min.

Chlorine inorganic anions (Cl⁻, ClO⁻, ClO₂⁻, ClO₃⁻, ClO₄⁻) were determined by ion chromatography using a Shimadzu LC-20A equipped with a Shodex IC I-524A column; mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 10⁻³ dm³ min⁻¹ (concentration accuracy: ±0.5%; detection limit: 7 µg dm⁻³). The peak corresponding to hypochlorite interferes with that of chloride; therefore, the determination of hypochlorite was carried out by titration with 0.001 M As₂O₃ in 2.0 M NaOH, a selective redox titration [39, 40]. Inorganic chloramines were measured following the DPD (N,N-diethyl-phenylenediamine) standard colorimetric method described elsewhere [38]. This is a selective method for inorganic chloramines that allows to determine the presence of mono-, di- and trichloramine without the interferences of other oxidizing species formed during the process, such as, ozone, hydrogen peroxide...

Occurrence of trihalomethanes (CHCl₃, CHBrCl₂, CHBr₂Cl, CHBr₃) was followed by gas chromatography with an electron capture detector (ECD). The column used was a SPB 10 column (30 m x 0.25 mm; macroporous particles with 0.25 µm diameter). The flow rate was 50 mL min⁻¹ and the initial temperature was 50°C during 5 minutes until

reach a final value of 150°C (6°C min⁻¹). Injection volume was set to 1 µL during 5 minutes and hydrogen was used as carrier gas.

Results and Discussion

Figure 2 shows the disinfection of the effluent of a WWTP with a DiaCell ® 1001 equipped with three modules (six monopolar BDD anodes). This experiment has been carried out at a very low current density ($I=0.05$ A; $j=0.11$ mA cm⁻²) in order to try to prevent the formation of chlorates or perchlorates [27, 28]. It is important to state that the initial concentration of *E. coli* in the raw wastewater is not very high, especially as compared to those observed in other works found in the literature about the disinfection of wastewater for reclamation. However, it is characteristic of this effluent [41, 42] and it indicates a very good performance of the biological stage of the WWTP, perhaps related to a high operation sludge age of this bioreactor, which attains a previous sort of digestion of microorganisms.

As expected according to previous literature, disinfection is very efficient despite the low current intensity applied. This is a very important observation because it means that very low current charge applied is high enough to deplete pathogens from a real wastewater (even the last experimental point was not shown because of the nil value cannot be plotted in semi-logarithmic scale). The decrease is almost linear in semi-logarithmic plot except for a small plateau observed for current charge applied in the range 0.005-0.01 Ah dm⁻³. The removal of microorganisms can take place by different mechanisms: 1) The direct oxidation on the anode surface and 2) the formation of disinfectant species from the electrolysis of the ions contained in wastewater and, the subsequent attack to microorganisms (indirect oxidation). The first one takes place over

specific anode materials such as carbon cloth or felt whereas the second mechanism is favored with BDD anodes [43-45].

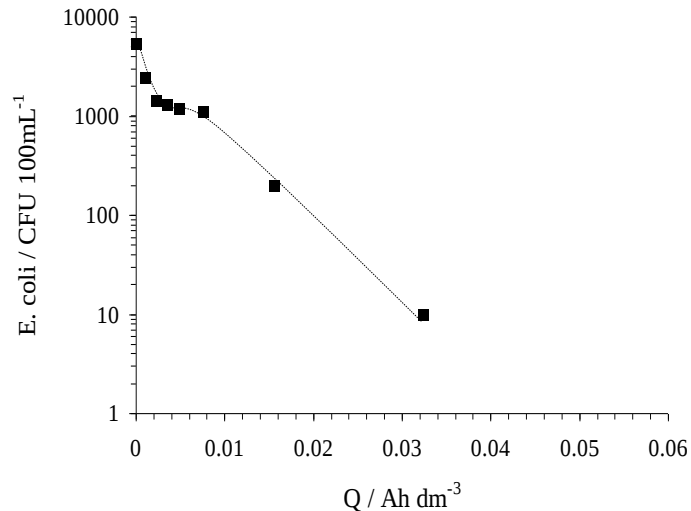
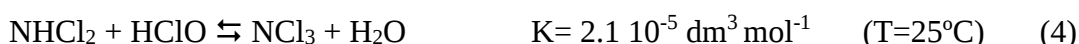
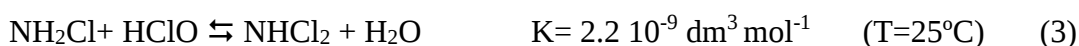
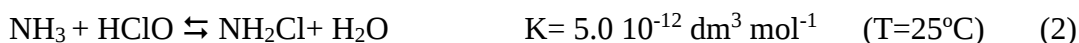


Figure 2. Disinfection of treated wastewater with the DiaCell® 1001 equipped with 3 modules. I: 0.05 A; q: 50 dm³ h⁻¹; T: 25°C; Anode: BDD; cathode: SS.

Figure 3 shows the main disinfectant species produced in the reaction media during the electrolysis. Initial concentration of chloride in raw wastewater is 165 mg dm⁻³. As it can be observed, only hypochlorite is formed in the electrolyte and its concentration reaches a maximum and then it decreases down to zero, meanwhile chloramines start to increase. At any case, concentration measured is very low as compared to the concentration of the raw chloride ion.

Concentration of ammonium in the raw wastewater is nil because of a very efficient nitrification stage in the secondary biological reactor. Opposite, the concentration of nitrate is significant because the WWTP has no denitrification stage (and hence the effluent of the biological reactor and influent to this disinfection process contains 8.72 mg dm⁻³ in the raw wastewater). Nitrate is known to be reduced cathodically to

ammonium (eq. 1) [30, 46] and this latter species reacts with hypochlorous acid to form sequentially monochloramine, dichloramine, nitrogen chloride (eqs. 2 to 4) and then gaseous nitrogen and chloride according to the well-known reactions [30].



This formation of chloramines is clearly observed in part (b) of Figure 3. Low concentration of hypochlorite and the very efficient reaction with ammonium helps to understand the nil occurrence of THMs (CHCl_3 , CHBrCl_2 , CHBr_2Cl , CH_3Br), checked in all the experiments carried out in this work.

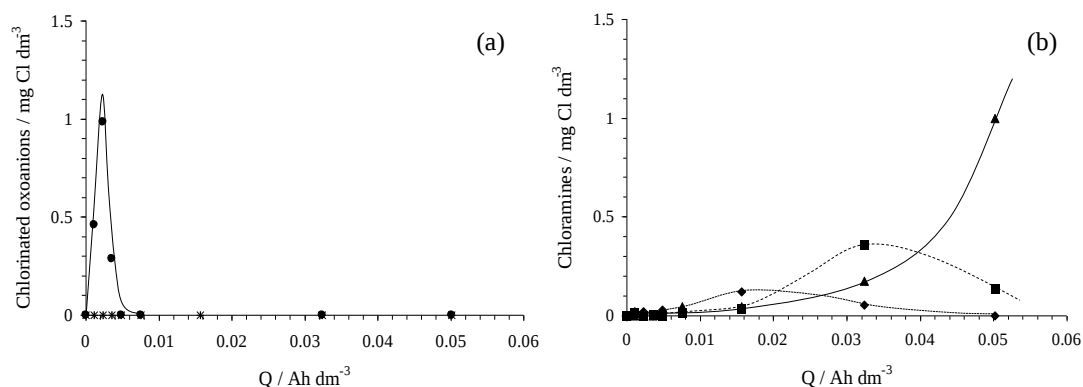


Figure 3. Production of disinfectant reagents and by-products with DiaCell® 1001 equipped with 3 modules (■ NH_2Cl ; ◆ NHCl_2 ; ▲ NCl_3 ; ● hypochlorite; * ClO_3^- ; + ClO_4^-). I: 0.05 A; q: $50 \text{ dm}^3 \text{ h}^{-1}$; T: 25°C ; Anode: BDD; cathode: SS.

Opposite to what it is observed with the oxidants produced, almost no changes are observed in the rest of species contained in wastewater. Thus, in concordance with the

low current density applied to the treated wastewater, it seems reasonable that low changes are produced in wastewater, what it is important for the latter reuse of water. At this point, it has to be taken into account that in order to reclaim wastewater it is important not to modify substantially their properties with the occurrence of hazardous species or unsuitable pHs.

Figure 4 focused on the changes in the main outcomes of the process. As it can be observed, a very small decrease in the total organic carbon (TOC) and total nitrogen (N_T), a slight increase in the conductivity and a small surprisingly (specially taking into account this increase in the conductivity) increase in the cell potential are the main changes. The most interesting change is the N_T because the last stage in the oxidation of ammonium with hypochlorite is the formation of nitrogen gas and hence it indicates the depletion of this species. The almost nil decrease in the TOC in comparison to the very efficient microorganisms' depletion (total disinfection) is explained in terms of the more efficient production of disinfection agents and the low amount of TOC in the bulk (mass transfer controlled process).

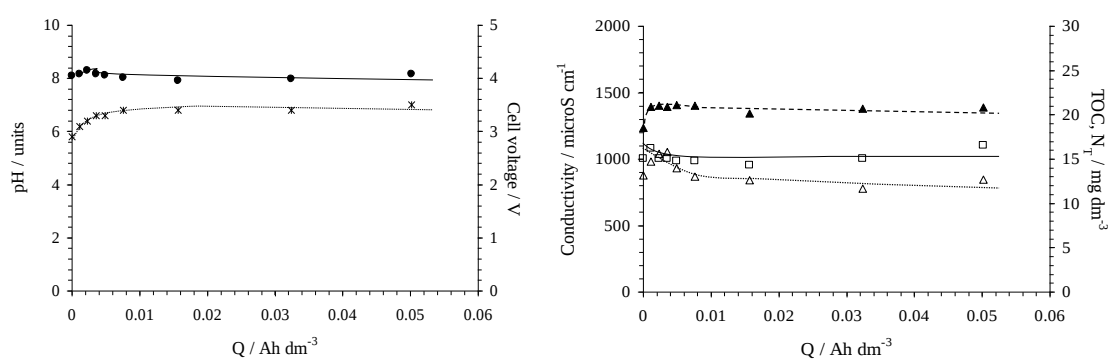


Figure 4. Disinfection of treated wastewater with theDiaCell® 1001 equipped with 3 modules ($\blacktriangle$ conductivity; $\square$ total nitrogen; $\triangle$ total organic carbon; $\bullet$ pH; $*$ cell voltage). I: 0.05 A; q: $50 \text{ dm}^3 \text{ h}^{-1}$; T: 25°C ; anode: BDD; cathode: SS.

Once the performance of the stack equipped with several monopolar electrodes has been studied, it is interesting to check the effect of the number of cells stacked on the efficiency of the disinfection. Figure 5 compares the disinfection attained by the stacks DiaCell Type 1001 equipped with different number of cells (and hence of electrodes). In every case, the same total current has been applied to the stacks (0.07 A) so the main difference is the current density, which becomes lower as the number of cells (and hence of electrodes) increases. As it can be observed, there is almost no effect of the number of cells stacked but simply the typical variability obtained in the disinfection of wastewater. In fact, the best and the worst results shown in the plot are obtained with two intermediate and very similar stacks (3 and 4 components). This observation supports the explanation and hence, the low effect of the number of cells staked with monopolar connection of the electrodes. It is an important observation because it means that ED with commercial DiaCell systems is a non-very complex process and that there cannot be expected great differences between the results obtained in lab scale and in higher scale studies [27, 28].

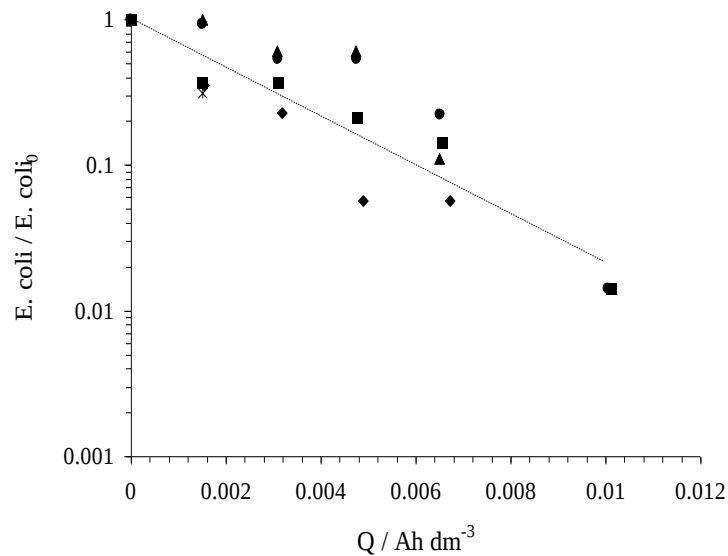


Figure 5. Disinfection with the DiaCell® 1001 equipped with 1 module (●); 2 modules (■); 3 modules (◆); 4 modules (▲) and 5 modules (*). I: 0.07 A; q: 50 dm³ h⁻¹; T: 25°C; anode: BDD; cathode: SS.

Regarding the comparison between the connection of electrodes, Figure 6 compares the performance of the complete stack of DiaCell® type 401 and DiaCell® type 1001 for three different external intensities (in the DiaCell® type 401 there is bipolar connection of electrodes). Clearly, type 401 is much more efficient than type 1001 and hence this type of cell is shown to be a very good candidate for this type of disinfection processes. Results obtained at 0.05 and 0.07 A are comparable in both configurations (the type 401 and the type 1001). However, results obtained at the lowest tested current density are completely different: higher efficiency for the type 401 and clearly lower efficiency for the type 1001. In order to explain these differences, it is interesting to study the changes in the operating parameters and oxidant species formed during the different electrolyses.

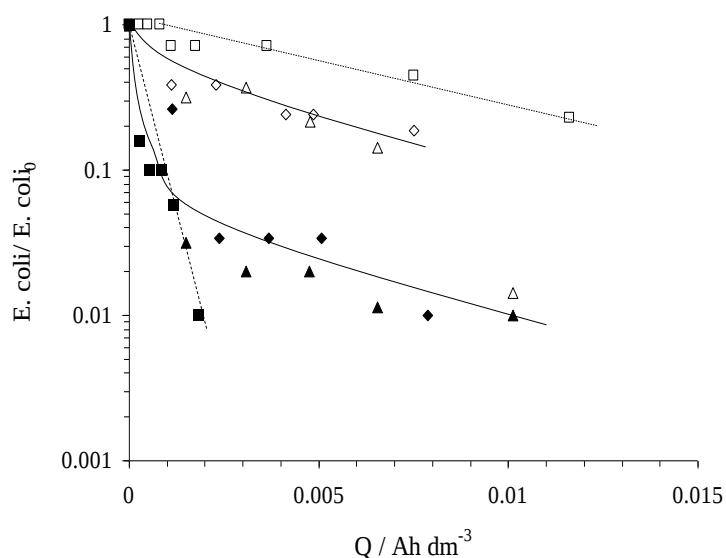


Figure 6. Comparison of the disinfection carried out by a complete module DiaCell® type 401 (full symbols) equipped with bipolar electrodes and DiaCell® type 1001

equipped with monopolar electrodes (empty symbols) (■, □ 0.01 A; ◆, ◇ 0.05 A; ▲, △ 0.07 A). q : 50 dm³ h⁻¹; T: 25°C; anode: BDD; cathode: SS.

Figure 7 and 8 show the maximum concentration of hypochlorite, chloramines and nitrogen chloride produced with both stacks as a function of the total current intensity applied. The experimental data are adjusted to a characteristic breakpoint chlorination for the systems without organic matter. As it can be observed, the concentrations attained are very low, especially as compared to the concentration of chlorides contained in the raw wastewater, and they never surpass the 0.4 mg dm⁻³ level. They are comparable in terms of total chloride oxidized, both in the case of the stack equipped with monopolar electrodes (DiaCell 1001) and in the stack equipped with bipolar electrodes, although speciation is completely different. This fact supports the different reactivity in both systems. Thus, in observing deeper the figures, it can be seen that hypochlorite is contained in high concentrations only in the tests with DiaCell 1001 stack while in the tests with the bipolar stack its concentration is almost nil. Opposite, the concentration of chloramines is much higher in the case of the bipolar stack and increases with the current intensity in the case of the DiaCell 1001. In addition, it is important to point out that concentration of hypochlorite does not increase but decrease with the total intensity. Both, the decrease of concentration with the DiaCell 1001 and the depletion with the DiaCell 401 can be explained by the formation of chloramines. To understand this improved formation of chloramines, it has to be taken into account the cathodic reduction of nitrates to ammonium ions, which was promoted operating at higher cell voltages (higher intensity and or/ bipolar connection). The higher efficiency of the bipolar system indicates that these chloramines, together with hypochlorite, are playing a very important role in the complete disinfection of the waste. Hence, in

comparing the experiments carried out at 0.01 A (the most different in the comparison shown in Figure 6) it can be seen than in the case of the type 1001, hypochlorite is the main species with a very high concentration while in the case of type 401 the most remarkable observation is the high concentration of monochloramine.

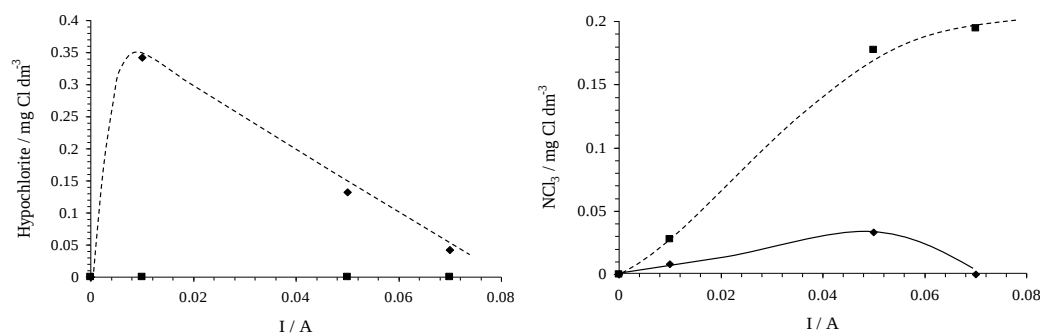


Figure 7. Maximum concentration of hypochlorite and nitrogen trichloride detected during the electrolysis of wastewater with the ■ DiaCell type 401(bipolar connection of electrodes) ◆ DiaCell type 1001 (monopolar connection of electrodes). I: 0.01 A; q: 50 dm³ h⁻¹; T: 25°C; anode: BDD; cathode: SS (monopolar) / BDD (bipolar).

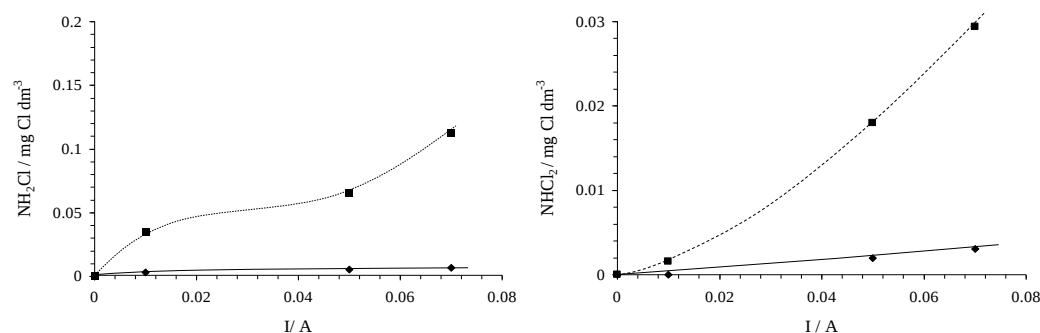


Figure 8. Maximum concentration of monochloramine and dichloramine detected during the electrolysis of wastewater with the ■ DiaCell type 401(bipolar connection of electrodes) ◆ DiaCell type 1001 (monopolar connection of electrodes). I: 0.01 A; q: 50 dm³ h⁻¹; T: 25°C; anode: BDD; cathode: SS (monopolar) / BDD (bipolar).

electrodes) ♦ DiaCell type 1001 (monopolar connection of electrodes). I: 0.01 A; q: 50 dm³ h⁻¹; T: 25°C; anode: BDD; cathode: SS (monopolar) / BDD (bipolar).

Finally, Figure 9 informs about a very important parameter: the cell voltage. All the experiments were carried out galvanostatically and hence the cell voltage is an output. As it can be observed, there is not a significant change in its value during each electrolysis, indicating no changes in the electrodes surfaces during the disinfection. In comparing the different tests carried out, it can be seen that resulting values increase with the current applied. Obviously, the DiaCell type 401 shows a much higher increase due to the use of bipolar electrodes while for DiaCell type1001 the increase caused by operating at higher intensities is much lower. Furthermore, these differences observed between both stacks are related to the cathode material. In this context, the Tafel slope for the hydrogen evolution reaction (HER) on BDD cathode is much greater than that for stainless steel. These increases reflect on the operating cost.

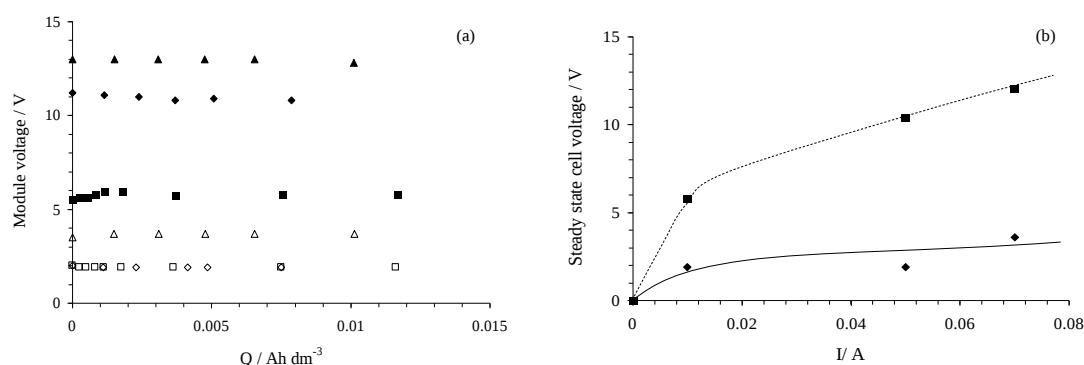


Figure 9. Changes in the module voltage during electrolysis (a) and influence of the intensity on the steady state cell voltage (b) in both stacks. (■,□) 0.01; (◆,◇) 0.05 A; (▲,△) 0.07 A. Full symbols: bipolar; empty symbols: monopolar

This is clearly seen in comparing the energy consumption, which can be calculated from the values of the electric charge passed (Q) and the total applied voltage (V) for each stack (eq. 5).

$$W \text{ (kWh m}^{-3}\text{)} = Q \cdot V \quad [5]$$

Table 2 shows the results obtained in the calculations carried out at three different current intensities for the total removal of microorganisms. It can be seen that for very low current densities the bipolar choice is the best option while at higher values, the DiaCell 1001 stack becomes the most efficient choice.

Table 2. Energy consumption.

Current intensity (A)	DiaCell type 1001 (monopolar)	DiaCell type 401 (bipolar)
0.01	Q: 0.012 Ah dm ⁻³ V: 1.9 V W: 0.023 kWh m ⁻³	Q: 0.002 Ah dm ⁻³ V: 5.9 V W: 0.012 kWh m ⁻³
0.05	Q: 0.050 Ah dm ⁻³ V: 1.9 V W: 0.095 kWh m ⁻³	Q: 0.008 Ah dm ⁻³ V: 10.8 V W: 0.086 kWh m ⁻³
0.07	Q: 0.021 Ah dm ⁻³ V: 3.7 V W: 0.078 kWh m ⁻³	Q: 0.010 Ah dm ⁻³ V: 12.8 V W: 0.128 kWh m ⁻³

Conclusions

From this work, the following conclusions can be drawn:

- Electro-disinfection with diamond electrodes of the effluents of secondary treatment is very effective. Low current charges applied are required to attain a total depletion of living *E. coli*, regardless of the number of electrodes contained in the stacks and the type of connection used.
- The production of disinfectant reagents from the species contained in wastewater and the prevention in the formation of hazardous species like chlorates and perchlorates are favored at low current densities.
- Hypochlorite and chloramines are the primary species formed. The stack equipped with bipolar electrodes promotes the higher formation of chloramines while the stack equipped with monopolar electrodes promotes the formation of hypochlorite at low current densities and chloramines at high current densities. Speciation can be explained in terms of the production of ammonium from the nitrates contained in the raw wastewater.

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